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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1]A manufacturing method of a lithium sulfide making lithium hydroxide and hydrogen sulfide react in an aprotic organic solvent, generating a water lithium sulfide, desulfurization--ization-hydrogenating this reaction liquid subsequently and generating a lithium sulfide.

[Claim 2]A manufacturing method of the lithium sulfide according to claim 1, wherein reaction temperature at the time of generation of said water lithium sulfide is 0-150 ** and reaction temperature at the time of said desulfurization-ized hydrogenation is 150-200 **.

[Claim 3]A manufacturing method of the lithium sulfide according to claim 1 or 2 distilling off water which carries out subraw at the time of generation of said water lithium sulfide.

[Claim 4]A manufacturing method of a lithium sulfide making lithium hydroxide and hydrogen sulfide react in an aprotic organic solvent, and generating a lithium sulfide directly.

[Claim 5]A manufacturing method of the lithium sulfide according to claim 4, wherein reaction temperature at the time of generation of said lithium sulfide is 150-200 **.

[Detailed Description of the Invention]**[0001]**

[Industrial Application]This invention relates to the manufacturing method of a lithium sulfide. It is especially related with the manufacturing method of a useful lithium sulfide as synthetic materials of detailed poly ARIRENSURUFIDO suitably used in electricity, the electronic field, and the high rigidity material field.

[0002]

[Description of the Prior Art]heating simple substance lithium and sulfur more than the melting point, and a lithium sulfide making them react, and forming it conventionally (Troost L. Ann. Chim. Phys., 1875, and v.51 (3).) p. It returned and formed with carbon, hydrogen, or

ammonia, heating 103 and lithium sulfate (KE VE Samsonov, sulfide manual-physical-properties written by S VE Drozdova, and constitutional diagram -).

[0003]

[Problem to be solved by the invention]However, the conditions in such a conventional method had to be very severe, therefore the process had to be a firm thing which can bear complicated and severe conditions. This invention is made in view of an above-mentioned problem, and is a thing.

The purpose is to provide the manufacturing method of the lithium sulfide which can obtain the lithium sulfide of high purity as be alike.

[0004]

[Means for solving problem]In order to attain the above-mentioned purpose, according to this invention, the manufacturing method of the lithium sulfide making lithium hydroxide and hydrogen sulfide react in an aprotic organic solvent, generating a water lithium sulfide, desulfurization--ization-hydrogenating this reaction liquid subsequently and generating a lithium sulfide is provided.

[0005]The manufacturing method of a lithium sulfide, wherein the reaction temperature at the time of generation of said water lithium sulfide is 0-150 ** and the reaction temperature at the time of said desulfurization-ized hydrogenation is 150-200 ** as the desirable mode is provided.

[0006]The manufacturing method of the lithium sulfide distilling off the water which carries out subraw is provided at the time of generation of said water lithium sulfide.

[0007]Lithium hydroxide and hydrogen sulfide are made to react in an aprotic organic solvent, and the manufacturing method of the lithium sulfide generating a lithium sulfide directly is provided.

[0008]The manufacturing method of the lithium sulfide characterized by the reaction temperature at the time of generation of said lithium sulfide being 150-200 ** as the desirable mode is provided.

[0009]Hereafter, this invention is explained concretely, referring to following drawing 1.

1. In the invention of the first of the generation application concerned of the first invention (1) water lithium sulfide (LiSH), as mentioned above, make lithium hydroxide and hydrogen sulfide react in an aprotic organic solvent, and generate a water lithium sulfide (LiSH) first.

**, [as an aprotic organic solvent used for aprotic organic solvent this invention] Generally, aprotic polar organic compounds (for example, an amide compound, a lactam compound, a urea compound, an organic sulfur compound, a ring type organophosphorus compound, etc.) can be conveniently used as an independent solvent or a mixed solvent.

[0010][among these aprotic polar organic compounds] [as said amide compound] For

example, N and N-JIMECHIRU formamide, N, and N-JIECHIRU formamide, N, and N-JIMECHIRU aceto amide, N, and N-JIECHIRU aceto amide, N, and N-JIPURO pill aceto amide, N, and N-dimethylbenzoic acid amide **** can be mentioned.

[0011]As said lactam compound, for example, Caprolactam, N-methyl caprolactam, N-ARUKIRU caprolactam, such as N-ethyl caprolactam, N-isopropyl caprolactam, N-isobutyl caprolactam, N-norm RUPURO pill caprolactam, N-NORUMARU butyl caprolactam, and N-cyclohexyl caprolactam, An N-methyl 2-pylori boss (NMP), An N-ethyl 2-pylori boss, an N-isopropyl 2-pylori boss, an N-isobutyl 2-pylori boss, an N-NORUMARU propyl 2-pylori boss, an N-NORUMARU butyl 2-pylori boss, an N-cyclohexyl 2-pylori boss, an N-methyl 3-methyl 2-pylori boss, An N-ethyl 3-methyl 2-pylori boss, the N-methyl 34, a 5-bird methyl 2-pylori boss, N-methyl 2-PIPERIDON, N-ethyl 2-PIPERIDON, N-isopropyl 2-PIPERIDON, N-methyl 6-methyl 2-PIPERIDON, N-methyl 3-ethyl 2-PIPERIDON etc. can be mentioned.

[0012]As said urea compound, tetramethyl urea, N, and N'- JIMECHIRU ethylene urea, N, N'- JIMECHIRU propylene urea etc. can be mentioned, for example.

[0013]As said organic sulfur compound, dimethyl sulfoxide, JIECHIRUSURUHOKISHIDO, diphenylsulfone, a 1-methyl 1-oxo sulfo run, a 1-ethyl 1-oxo sulfo run, a 1-phenyl 1-oxo sulfo run, etc., for example again, As said ring type organophosphorus compound, a 1-methyl 1-oxo phospho run, a 1-NORUMARU propyl 1-oxo phospho run, a 1-phenyl 1-oxo phospho run, etc. can be mentioned, for example.

[0014]It is kind independent, respectively, or two or more sorts can be mixed, it can mix with other solvent ingredients which do not have trouble in the purpose of this invention further, and an aprotic polarity organic compound of these various kinds can be used as said aprotic organic solvent.

[0015]Also in said various kinds of aprotic organic solvents, N-ARUKIRU caprolactam and N-ARUKIRU pylori boss are preferred, and especially a desirable thing is an N-methyl 2-pylori boss.

[0016]** As lithium hydroxide used for lithium hydroxide this invention, there is no restriction in particular, and as long as it is high purity, a commercial product can be used.

[0017]** There is no restriction in particular as hydrogen sulfide used for hydrogen sulfide this invention.

[0018]** Use rates (a molar ratio: lithium hydroxide/hydrogen sulfide) of lithium hydroxide to use rate hydrogen sulfide are usually 1.80-3.00, especially 1.95-3.00. If a use rate of lithium hydroxide to hydrogen sulfide is in said within the limits, a reaction will advance still more smoothly.

[0019]** Throw in said aprotic organic solvent and lithium hydroxide in a reaction vessel, and make hydrogen sulfide blow in and react to preparation liquid obtained next in reaction this invention of lithium hydroxide and hydrogen sulfide. In this case, lithium hydroxide may be

made to mix and react to aprotic solvent solution which blew hydrogen sulfide beforehand into an aprotic organic solvent and in which it was made to dissolve.

[0020] Pressure at the time of blowing hydrogen sulfide may also pressurize normal pressure. It is preferred for there to be no restriction in particular and to usually consider it as about 10 to 180 minutes as blowing-in time. It is preferred for restriction in particular not to have blowing-in speed, either, and to usually make it into a 10-1000-cc part grade for /. Restriction in particular does not have how to blow hydrogen sulfide, either, for example, lithium hydroxide in an N-methyl 2-pylori boss, [in churning, for example, a 500 ml glass separable flask,] A method usually used, such as carrying out babbling of the gas-like hydrogen sulfide into it, can be used agitating at 300-700 rpm using disk turbine wings as churning wings. In this case, water may exist.

[0021] As for the reaction temperature in this case, 0-150 °C is preferred, and its 120-140 °C is still more preferred. Since reaction velocity becomes remarkably slow that it is less than 0 °C, if the time concerning composition becomes long, becomes uneconomical on a process and exceeds 150 °C, hydrogen sulfide will become difficult to melt into solution, and, as a result, the increase of the amount of wells of hydrogen sulfide and absorption efficiency will worsen. Although the amount of supply of hydrogen sulfide may be extracted in order to prevent it, if it does so, reaction time becomes long and is uneconomical on a process.

[0022] As for reaction time, it is preferred to make it beyond the value acquired by breaking the amount of required hydrogen sulfide computed from the use rate of said hydrogen sulfide at the speed which the hydrogen sulfide to supply does not blow. The purity of the lithium sulfide obtained by hydrogen sulfide running short that it is less than [it] stoichiometrically to lithium hydroxide falls (lithium hydroxide of materials is intermingled in a lithium sulfide).

[0023] Thus, by throwing in hydrogen sulfide, the lithium hydroxide which existed by the shape of a solid in the system dissolves in the fluid portion in a system.

[0024] (2) In generation this invention of a lithium sulfide (Li_2S), desulfurization--ization-hydrogenate the water lithium sulfide (LiSH) in the reaction liquid, and generate the lithium sulfide (Li_2S) of high purity, after generating a water lithium sulfide as mentioned above.

[0025] As for the reaction temperature at the time of performing this desulfurization-ized hydrogenation, 150-200 °C is preferred, and its 170-190 °C is still more preferred. Reaction velocity is remarkably slow in it being less than 150 °C, and if it exceeds 200 °C, the boiling point of a solvent may be exceeded, desulfurization-ized hydrogen time becomes long, and is uneconomical on a process, use of a pressure vessel is needed for composition, and it is uneconomical.

[0026] About reaction time, 0.3 to 6 hours is preferred and 0.5 to 2 hours is still more preferred. If reaction time runs short that it is less than 0.3 hour, a water lithium sulfide is intermingled in a product, the fall of the purity of a lithium sulfide is caused and it exceeds 6 hours, reaction

time becomes long, leads to enlargement of a reaction vessel, and is uneconomical on a process.

[0027]It is preferred to arrange a capacitor in the reaction vessel upper part in order to distill off the water which carries out subraw at the time of generation of a water lithium sulfide. It is because the hydrolysis reaction of the lithium sulfide obtained while barring advance of a reaction will occur if water exists.

[0028]2. Generate said lithium hydroxide (Li_2S) in said aprotic organic solvent as mentioned above in the invention of the second of the second invention application concerned. Therefore, in this 2nd invention, the process of generating a water lithium sulfide (LiSH) is not needed in the middle, but Li_2S can be generated at one process.

[0029]150-200 °C is preferred and, as for the reaction temperature in this case, 170-190 °C is still more preferred. The purity of the increase of the rate of stream-ized lithium and a lithium sulfide falls [the substance obtained as it is less than 150 °C]. If it exceeds 200 °C, the boiling point may be exceeded depending on a solvent, use of a pressure vessel is needed for composition, and it is uneconomical.

[0030]Reaction time is the same as that of the case of generation of the lithium sulfide in the first invention, and it is preferred to make it beyond the value acquired by dividing at the speed which the hydrogen sulfide which supplies the amount of required hydrogen sulfide does not blow.

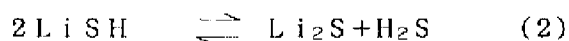
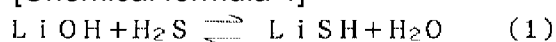
[0031]The same thing as the case in the first invention can be used for materials, a reaction vessel, etc. to be used.

[0032]

[Function]At the desulfurization-ized hydrogenation process of the first invention, the point which has not blown hydrogen sulfide has the main differences with the invention of the first of an application concerned, and the second invention. If it puts in another way, it is in the point whether the process denoted by the chemicals stoichiometry type shown in the following-ization 1 is performed at two processes, or to carry out at one process.

[0033]

[Chemical formula 1]



[0034]That the lithium sulfide of high purity is obtained by this invention, in the first invention, the above (1) and (2) types are static reaction.

It is because a reaction can be advanced efficiently by removing suboutput, H_2O , and H_2S out of a system.

In the second invention, in the first invention, composition was 2 process necessity, but it is because the above-mentioned (2) formula is made to react alternatively, 1 process-ization is attained and Li_2S can be obtained efficiently by controlling reaction temperature.

[0035]

[Working example] Hereafter, a work example explains this invention still more concretely.

[Work example 1] A 3326.4 g (33.6 mol) N-methyl 2-pylori boss (NMP) and 287.4 g (12 mol) lithium hydroxide were taught to 10-l. autoclave with churning wings, and it ****(ed) at 300 rpm and 130 **. Hydrogen sulfide was blown with the speed of supply of 3 l. / min. after **** and into liquid for 2 hours. Under [a fixed quantity / concentration / sulfur and / Li / it samples a part of this reaction liquid and]. Iodometry (after adding dilute hydrochloric acid to sample liquid, superfluous I_2 solution is added and back titration of the I_2 solution for an excess is carried out with sodium subsulfite standard solution) analyzed sulfur concentration, and the ion chromatogram analyzed Li concentration. As a result, it was sulfur/Li=0.996 (molar ratio). As a result, it turns out that LiSH was obtained in high purity. Then, bottom (200cc/min.) **** of a nitrogen air current of this reaction liquid was carried out, and some hydrogen sulfide which reacted was desulfurization--ization-hydrogenated. The water which carried out subraw by the reaction of the above-mentioned hydrogen sulfide and lithium hydroxide began evaporation as it ****(ed), but this water was condensed by the capacitor and extracted out of the system. While distilling off water out of the system, although the temperature of reaction liquid rose, when it amounted to 180 **, it stopped ****, and held it to constant temperature. The relation between the temperature in reaction liquid in the meantime and sulfur concentration was shown in the following table 1. As a result, it turns out that the desulfurization-ized hydrogen reaction was completed and Li_2S was obtained in high purity in about 50 to 80 minutes. Obtained Li_2S became clear [also existing stably (about 3 hours) under 180 ** in a solvent].

[0036]

[Table 1]

----- Reaction conditions (desulfurization yellow reaction) Analysis result Time
 Reaction solution temperature S/Li min. ** mol ratio. ----- -- 0 1300.996 25 177 0.776
 50 183 0.565 80 181 0.498 110 182 0.499 175 180 0.498 -----[0037] After the above-mentioned reaction, the lithium sulfide deposited in the solvent as a solid. Filtration under reduced pressure of the content was opened and carried out to glass filters (G4) after cooling. Then, the solid was washed 3 times in NMP, and also acetone washed twice, and the yield was measured after drying. As a result, it was 92% of yield at the time of presupposing that all lithium hydroxide of preparation changes into a lithium sulfide. When the X diffraction of the obtained white powder was carried out, the lithium sulfide and its diffraction peak of the reagent (purity: not less than 99.8%) were completely in agreement.

[0038][a work example 2] -- using the completely same reaction apparatus as a work example 1 -- NMP3336g (33.7 mol) -- and lithium-hydroxide 479g (20 mol) taught, and ****(ed) at 300 rpm, and an internal temperature was held at 190**5 **. And hydrogen sulfide was blown in 1 l. / min. for 6 hours. In the meantime, water which carries out subraw was distilled off like a work example 1. After a reaction, a lithium sulfide deposited in a solvent as a solid. Filtration under reduced pressure of the content was opened and carried out to glass filters (G4) after cooling. Then, a solid was washed 3 times in NMP, and also acetone washed twice, and a yield was measured after drying. As a result, it was 90% of yield at the time of presupposing that all lithium hydroxide of preparation changes into a lithium sulfide. When the X diffraction of the obtained white powder was carried out, a lithium sulfide and its diffraction peak of said reagent were completely in agreement, and also it was sulfur/Li=0.505 (molar ratio). As a result, a lithium sulfide was obtained in high purity.

[0039]

[Effect of the Invention]As explained above, this invention, the lithium sulfide (Li_2S) of high purity can be obtained by a simple means. The effect that a lithium sulfide can be obtained efficiently and a lithium sulfide can be efficiently obtained only at one process in the second invention in the first invention in short-time reaction time is demonstrated collectively.

[Translation done.]